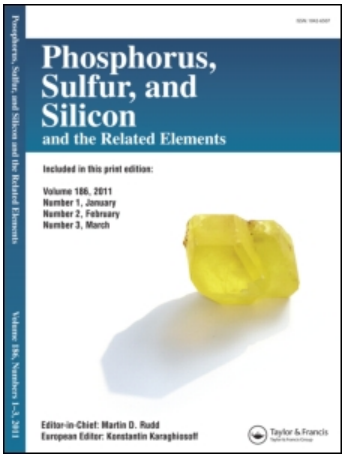


## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Novel Spiro Substituted Cyclotriphosphazenes Incorporating Ethylenedinitramine Units

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# NOVEL SPIRO SUBSTITUTED CYCLOTRIPHOSPHAZENES INCORPORATING ETHYLENEDINITRAMINE UNITS

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A new initiative directed toward understanding the chemistry, synthesis, and properties of non or low carbon-based energetic compositions was undertaken. Initial synthesis work focused on reactions of hexachlorocyclotriphosphazene **1**, with ethylenediamino and azido functional groups. The reaction of **1** with ethylenediamine, N,N′-dinitroethylenediamine, and N,N′-bis(trimethylsilyl)ethylenediamine yielded novel bis- and tris-spiro(ethylenediamino)cyclotriphosphazenes. Subsequent nitration with either nitronium tetrafluoroborate or nitric acid (100%) acetic anhydride gave various mono-, bis- and tris-spiro(N,N′-dinitroethylenediamino)cyclotriphosphazenes.

*Key words:* Cyclotriphosphazenes; nitramines; nitration; energetic compounds.

## INTRODUCTION

Considerable current interest has centered on the reactions of hexachlorocyclotriphosphazene, **1**, with difunctional reagents.[1] Of particular note are the biogenic

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diamines which offer potential application in the design of more selective antitumorals.[2] Difunctional reagents have been shown to react with **1** to give three different types of products: a) bino derivatives by the displacement of two chlorine atoms from phosphorus atoms in different rings leading to cyclolinear polymers, b) ansa compounds derived from the displacement of two chlorine atoms from different phosphorus atoms in the same ring and c) spiro derivatives formed by the displacement of chlorine atoms from the same phosphorus atom. A large number of substituted phosphazenes with bino and/or ansa and/or spiro configurations have been reported.[1,2]

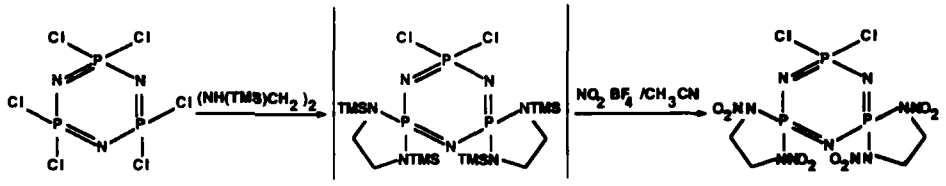
The reaction of **1** with 1,2-diaminoethane and 1,3-diaminopropane leads exclusively to spiro fused derivatives.[3] It is interesting to note that while treatment of **1** with an excess of 1,3-diaminopropane leads to the tris-spiro derivative,[4] only the mono-spiro product can be obtained in pure form from 1,2-diaminoethane. The bis-spiro compound was detected by $^{31}P$ NMR, while the tris-spiro adduct still remains unknown.[3c] The failure to isolate the bis-spiro and tris-spiro adducts has been attributed to the presence of reactive PNHR units on the mono-spirocyclotriphosphazene coupled with the reduced stability of five-membered spiro rings compared to six-membered congeners.[1,5] This hypothesis was reinforced by the observation that the reaction of **1** with an excess of N,N′-dimethylethylenediamine leads to the expected tris-spiro product containing only PNRR units.[6] We present here the results of our investigation of the reaction of **1** with N,N′-bis(trimethylsilyl)-ethylenediamine,[7] N,N′-dinitroethylenediamine, and 1,2-diaminoethane. The resulting products were converted to the novel 1,1,3,3,5,5-tris-spiro(N,N′-dinitroethylenediamino)cyclotriphosphazene compound which is of significant interest in energetic materials research.



## RESULTS AND DISCUSSION

Hexachlorocyclotriphosphazene, **1**, was treated with an excess of N,N′-bis(trimethylsilyl)ethylenediamine in refluxing tetrahydrofuran (THF) to give, after aqueous work-up, a product mixture containing principally 3,3,5,5-bis-spiro(N,N′-bistrimethylsilylethylenediamino)-1,1-dichlorocyclotriphosphazene, **2**. Compound **2** was consumed in a subsequent reaction step without further purification, Scheme 1. Nitration of this product with nitronium tetrafluoroborate in acetonitrile afforded 3,3-5,5-bis-spiro(N,N′-dinitroethylenediamino)-1, 1-dichlorocyclotriphosphazene, **3** (70% from **1**). No tris-spiro product was detected in the product mixture.

Alternatively, compound **3** was prepared by treating hexachlorocyclotriphosphazene with ethylenediamine by the method of Krishnamurthy *et al.*[3] to obtain




1 2 3

SCHEME 1

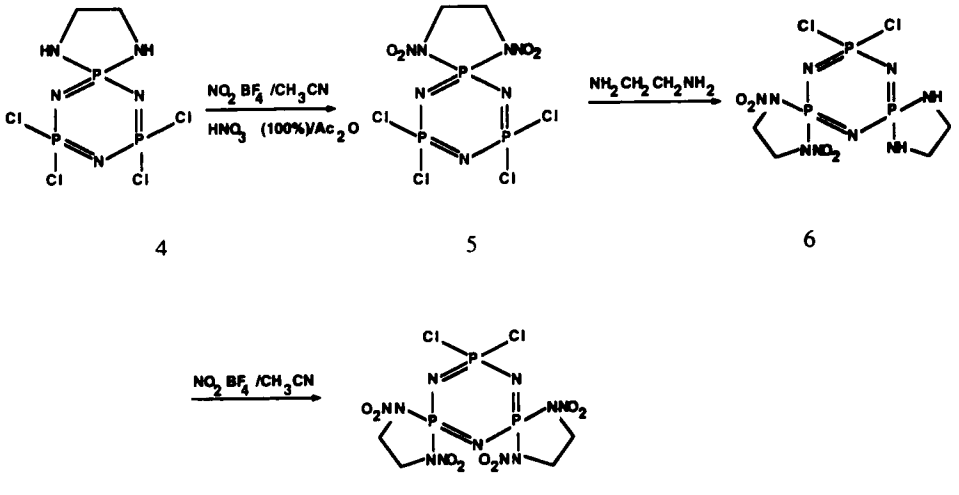
1,1-spiro(ethylenediamino)-3,3,5,5,-tetrachlorocyclotriphosphazene, **4**. Nitration of **4** was carried out using either nitronium tetrafluoroborate in acetonitrile or with an acetic anhydride/100% nitric acid mixture to give 1,1-spiro(N,N′-dinitroethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **5**. Brief treatment of **5** with an excess of ethylenediamine in methylene chloride gave 1,1-spiro(ethylenediamino)-3,3-spiro(N,N′-dinitroethylenediamino)-5,5-dichlorocyclotriphosphazene, **6**, which was nitrated with nitronium tetrafluoroborate to give **3**, Scheme 2.

Several attempts were made to add N,N′-dinitroethylenediamine (EDNA) or the corresponding disodium or dilithium derivatives to compound **1**. In all cases, no addition products were isolated. Attempts to add EDNA to the mono-spiro substituted cyclotriphosphazenes **4** and **5** also failed. It is assumed that the lack of reaction of EDNA and of its salts stem from the poor nucleophilicity of the nitramine moiety.

The proton decoupled $^{13}C$ NMR ($CDCl_3$) spectrum of compound **5** showed one signal at $\delta$ 41.4 (d, $J_{C-P}$ = 10.13 Hz), and $^{31}P$ NMR spectrum exhibited a triplet at $\delta$ −7.2 and a doublet at $\delta$ 28.6 ($J_{P-P}$ = 59.1 Hz). The proton decoupled $^{13}C$ NMR spectrum in acetone-$d_6$ of compound **3** showed a doublet at $\delta$ 42.1, and the $^{31}P$ NMR showed a doublet at $\delta$ 0.0 and a triplet at $\delta$ 38.0 ($J_{P-P}$ = 68.8 Hz). The structure of compound **3** was further confirmed by X-ray crystallography, Figure 1.

Addition of ethylenediamine to **3** was found to be slow. However, upon extended reflux (24 hr) a 84% yield of 1,1-spiro(ethylenediamino)-3,3,5,5-bis-spiro(N,N′-dinitroethylenediamino)cyclotriphosphazene, **7**, was realized. As depicted in Scheme 3, nitration of **7** with nitronium tetrafluoroborate proceeds smoothly to yield 1,1,3,3,5,5-tris-spiro(N,N′-dinitroethylenediamino)cyclotriphosphazene, **8**.

Compound **8** was also obtained from 1,1-spiro(N,N′-dinitroethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **5**. Treatment of compound **5**, with excess




4 5 6

3

SCHEME 2

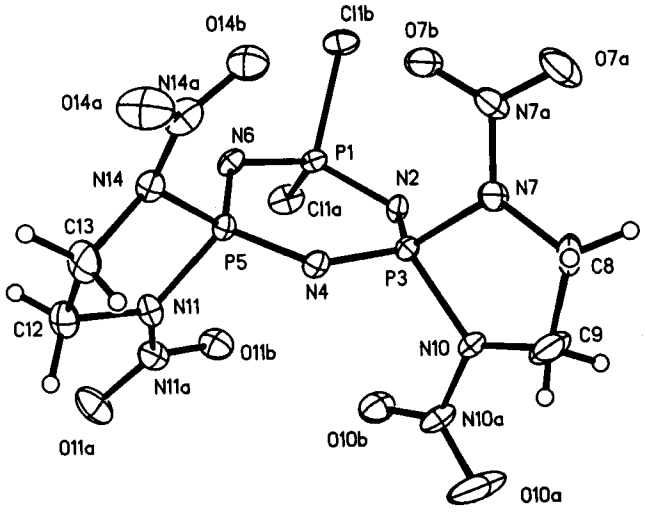
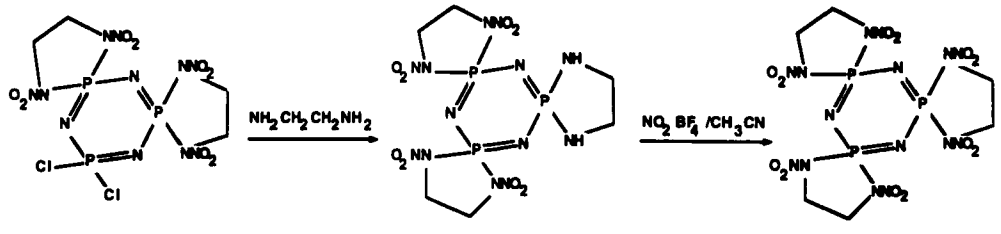
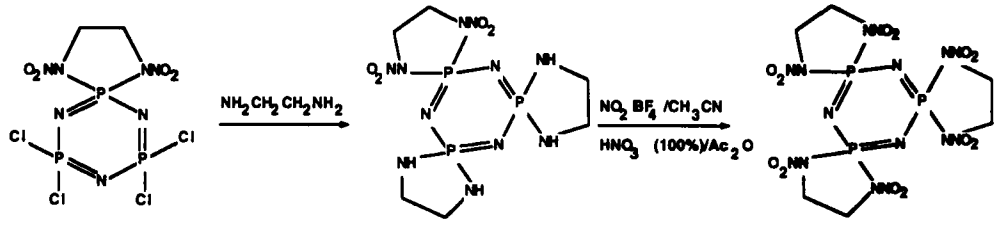



FIGURE 1 A thermal ellipsoid drawing showing the molecular structure and numbering scheme for 3,3,5,5-Bis-spiro(N,N′-dinitroethylenediamino)-1,1-dichlorocyclotriphosphazene, **3**.




3 7 8

SCHEME 3




5 9 8

SCHEME 4

ethylenediamine under reflux afforded 1,1-spiro(N,N′-dinitroethylenediamino)-3,3,5,5-bis-spiro(ethylenediamino)cyclotriphosphazene, **9**, in high yield after aqueous workup. Compound **8** was prepared in high yield by treating compound **9** with an acetic anhydride/100% nitric acid mixture, Scheme 4. The structure of the compound **8** was deduced on the basis of $^{13}C$ and $^{31}P$ NMR. Both exhibited a single signal attesting to the high symmetry of the molecule. The structure of **8** was further confirmed by X-ray crystallography, Figure 2.

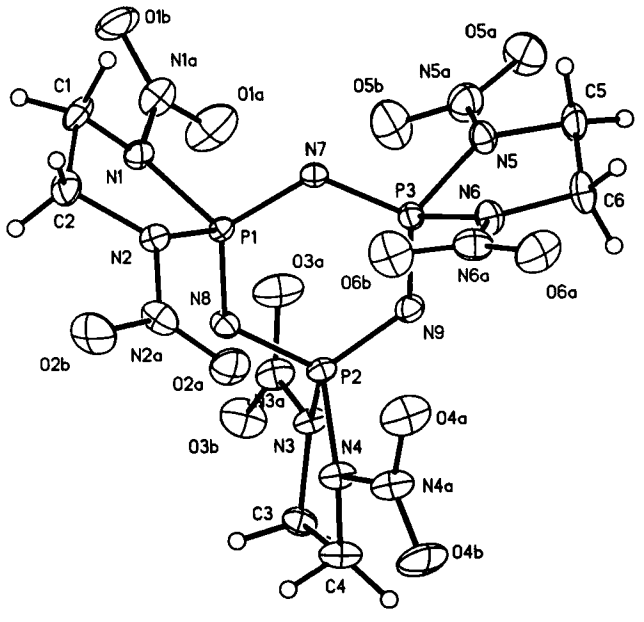


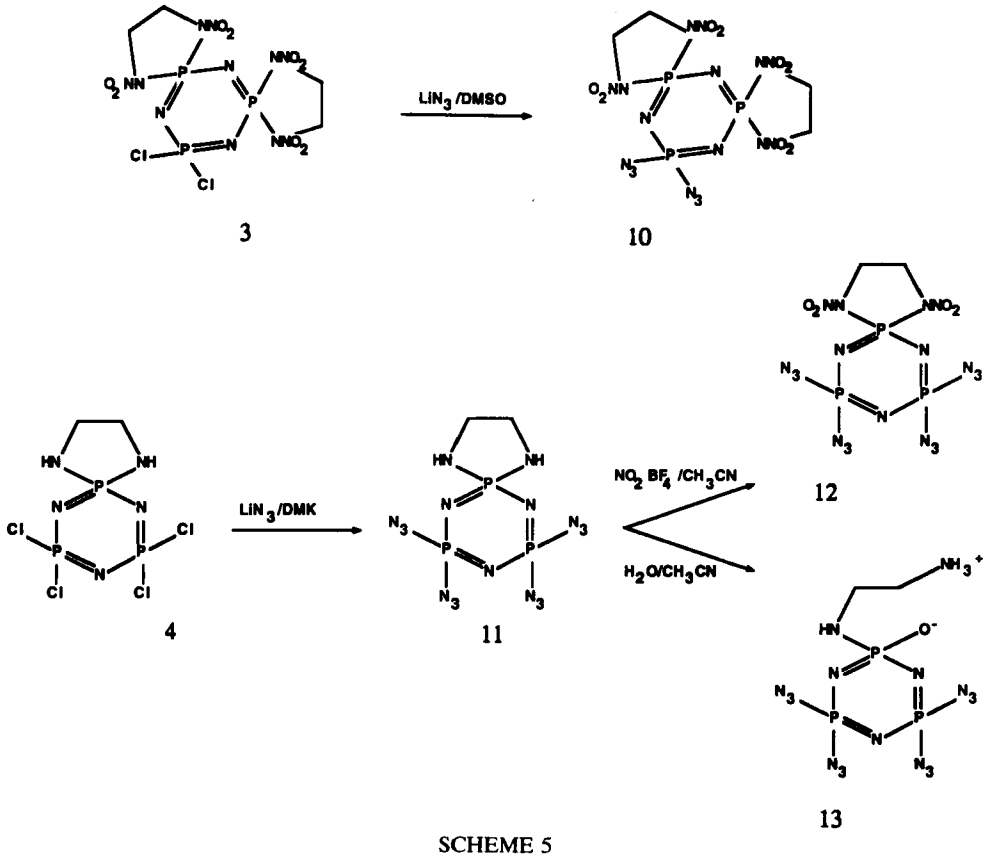

FIGURE 2 A thermal ellipsoid drawing showing the molecular structure and numbering scheme for 1,1,3,3,5,5-Tris-spiro(N,N′-dinitroethylenediamino)cyclotriphosphazene, **8**.

Nucleophilic azide displacement of the residual chloro groups in compounds **3** and **5** also was examined. Compound **3** was converted to the 1,1,3,3-bis-spiro(N,N′-dinitroethylenediamino)-5,5-diazidocyclotriphosphazene, **10**, by treatment with lithium azide in DMSO, Scheme 5. The corresponding 1,1-spiro(N,N′-dinitroethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **5**, did not yield the expected tetraazido compound **12** under similar conditions. Compound **12** was prepared by first converting **4** to the corresponding tetraazido compound **11** followed by nitration of **11** with nitronium tetrafluoroborate, Scheme 5.

A second product was isolated during our studies of the azide displacement reaction. If compound **11** was not converted immediately to the corresponding nitramine, or if compound **11** was treated with aqueous acetonitrile, a new compound was isolated. This material proved to be the 1-oxido compound **13** which resulted from ring opening of the N,N′-ethylenediamino moiety by water.

Compounds **3** and **8** represent the first examples of potentially useful energetic materials made from a cyclotriphosphazene nucleus. They have extremely high melting points, 242–244°C and 203–205°C, respectively, show no thermal instability in their DSC traces, and demonstrate impact and friction sensitivities similar to existing cyclic energetic nitramino material 1,3,5-trinitro-2,4,6-hexahydrotriazine (RDX). The azido substituted cyclotriphosphazenes proved to be extremely impact sensitive.[8] Extreme caution must be taken when working with these shock sensitive materials.

The X-ray crystal structure of compounds **3** and **8** gave measured densities of 1.898 and 1.887 g/cc, respectively. The density of the parent cyclotriphosphazene is 2.02[9] while that of N,N′-ethylenedinitramine is 1.71. The incorporation of both moieties enhanced the overall density of the resulting energetic material.




3 10 12 4 11 13

SCHEME 5

There are many reported crystallographic analyses of cyclotriphosphazenes. Examination of 47 well-determined ($R < 0.07$) amino-substituted cyclotriphosphazenes from the Cambridge Structural Database[10] indicated that the six PN ring bonds are statistically equal, with an average length of 1.592 Å, and that random deviations from this value are rather large (range: 1.55 to 1.67 Å). The average value for an *exo*-PN bond is 1.661 Å, also with a large range of variation, 1.59 to 1.72 Å. The bond distances in **3** and **8** are consistent with these values. However, all of the *exo*-PN bonds fall at the long end of the observed range, averaging 1.698 Å (range: 1.679 to 1.720 Å).

## EXPERIMENTAL

CAUTION! All polynitramine compounds are considered toxic and potentially explosive and should be handled with appropriate precautions. In all nitrations with nitronium tetrafluoroborate, upon removal of acetonitrile, ice cold water must be added immediately to the residue to quench any excess $NO_2BF_4$.

Melting points are uncorrected. NMR spectra were recorded on a Bruker NR 300 spectrometer. Chemical shifts are reported in ppm downfield from internal tetramethylsilane except for $^{31}P$ NMR spectra, which are referenced to phosphoric acid. THF was dried by distilling from benzophenone ketyl. Hexachlorocyclotriphosphazene was obtained from Aldrich Chemical Co. and nitronium tetrafluoroborate from Ozark-Mahoning, Inc. All spirocyclotriphosphazenes incorporating both NH and P—Cl linkages were found to be moisture sensitive and unstable in solution. These materials were used

immediately without further purification in subsequent reaction steps. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

*3,3,5,5-Bis-spiro(N,N'-dinitroethylenediamino)-1,1-dichlorocyclotriphosphazene*, **3**. A solution of hexachlorocyclotriphosphazene, **1** (20.0 g, 57.3 mmol) in dry THF (180 mL) was added dropwise to a refluxing solution of N,N'-bis(trimethylsilyl)ethylenediamine (60.0 g, 294 mmol) in THF (500 mL) under an inert atmosphere over 4 hours. The mixture was then stirred at reflux overnight. The resulting mixture was cooled to room temperature and concentrated under reduced pressure. Upon removal from the rotary evaporator, ice cold water (300 mL) was added immediately and the resulting cloudy solution extracted with methylene chloride (3 × 200 mL). The organic extracts were combined and dried over $MgSO_4$. The solution was then filtered and concentrated in vacuo to yield a viscous material.

The material obtained above was stirred in dry acetonitrile (500 mL) for 10 minutes. The suspension was then cooled in an ice bath (5–10°C) and nitronium tetrafluoroborate (31.3 g, 236 mmol) was added over a 10 minute period. The solution was stirred for another 2 hours at 5–10°C, and then concentrated under reduced pressure. To the residue ice cold water (800 mL) was immediately added and the mixture stirred for 30 minutes whereupon the product separated as a white solid and was collected by filtration. Recrystallization from aqueous acetone yielded **3** as a colorless solid (21.2 g, 73% from 1), mp 242–244°C.

Alternatively, $NO_2BF_4$ (1.5 g, 11.3 mmol) was added to an ice cooled solution of **6** (1.6 g, 3.8 mmol) in acetonitrile under dry nitrogen and the resulting solution was stirred at 0°C for an hour. The cooling bath was removed and stirring was continued overnight. The reaction mixture was then concentrated under reduced pressure and to the residue was immediately added ice cold water and methylene chloride. The organic phase was separated, washed successively with saturated $NaHCO_3$ solution, and saturated NaCl solution, then dried ($Na_2SO_4$), filtered and concentrated. The residue was chromatographed on silica gel using a 1:4 mixture of acetone/hexane eluent to give **3** (1.0 g, 2.0 mmol, 52%). CAUTION: compound **3** exhibits explosive behavior on heating.

IR (KBr), 1570 (N—$NO_2$), 1275 (N—$NO_2$), 1195 $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 4.25–4.50 (m); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 43.0 (br.); $^{31}P$ NMR (acetone-$d_6$) $\delta$ 0.0 (d), $\delta$ 38.0 (t, $J_{P-P}$ = 68.8 Hz). Anal. Calcd. for $C_4H_8{}^{35}Cl_2N_{11}O_8P_3$: $(M + H)^+$, 500.9147. Found: $(M + H)^+$, 500.9142.

*1,1-Spiro(N,N'-dinitroethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene*, **5**. To a cooled solution (5–7°C) of 1,1-spiro(ethylenediamino)-3,3,5,5-tetrachlorocyclotriphosphazene, **4** (1.6 g, 5 mmol) in acetonitrile (50 mL) was added nitronium tetrafluoroborate (1.5 g, 11.3 mmol) in one portion. The resulting suspension was stirred at 5–7°C for one hour and then stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure. The residue was taken up in methylene chloride (50 mL) and washed successively with water (50 mL), saturated $NaHCO_3$ solution (50 mL) and brine (50 mL). The organic phase was dried over $MgSO_4$, filtered and the filtrate was concentrated in vacuo to give a pale yellow solid. Recrystallization from acetone-hexanes afforded pure **5** as a colorless microcrystalline solid (1.1 g, 2.6 mmol, 52%), mp 225–227°C.

Alternatively, 100% nitric acid (3.0 g, 47.6 mmol) was added dropwise with stirring to acetic anhydride (7.39 g, 72.4 mmol) cooled to −5°C (salt-ice). The solution was then warmed to 20°C over 1 h, cooled again to −5°C, and to this was added **4** (1.0 g, 3.0 mmol) all at once. After stirring at −5°C for 1.5 h, the mixture was poured onto a mixture of ice and water (50 mL), and the precipitated white solid was filtered, washed with cold water and dried to give **5** (1.13 g, 89%): mp 223–226°C. Recrystallization from benzene-hexane gave colorless prisms: mp 225–227°C.

IR (KBr) 1575 (N—$NO_2$), 1275 (N—$NO_2$), 1210 $cm^{-1}$ (PNP); $^1H$ NMR ($CDCl_3$) $\delta$ 4.10 (d, $J_{P-H}$ = 6.6 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 41.0 (d, $J_{C-P}$ = 10.13 Hz); $^{31}P$ NMR ($CDCl_3$) $\delta$ −7.2 (t), $\delta$ 28.6 (d, $J_{P-P}$ = 59.1 Hz). HRMS EI $(M = H)^+$ Calcd. 422.8291; Found 422.8301. Anal. Calcd. for $C_2H_4Cl_4N_7O_4P_3$: C, 5.65; H, 0.95; Cl, 33.38; N, 23.08; P, 21.87. Found: C, 6.14; H, 0.95; Cl, 33.68; N, 22.47; P, 21.99.

*1,1-Spiro(ethylenediamino)-3,3-spiro(N,N'-dinitroethylenediamino)-5,5-dichloro-cyclotriphosphazene*, **6**. Ethylenediamine (1.0 g, 12.5 mmol) was slowly added to a stirred solution of **5** (0.05 g, 0.11 mmol) in methylene chloride (15 mL) at 25°C. The mixture was stirred at 25°C for one hour. A suspension was obtained and was extracted with water (60 mL). The organic layer was kept over $CaCl_2$ for one hour, filtered, and concentrated by rotary evaporator to yield **6** (0.04 g, 81%).

IR (KBr) 3400 (NH), 2890 (NH), 1550 (N—$NO_2$), 1270 (N—$NO_2$), 1230 (PNP) $cm^{-1}$; $^1H$ NMR (acetone-$d_6$) $\delta$ 2.81 (d), 3.45 (m), $\delta$ 4.10 (d, $J_{C-P}$ = 10.5 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 41.3 (d, $J_{C-P}$ = 9.0 Hz), 42.1 (d, $J_{C-P}$ = 10.5 Hz).

*1,1-Spiro(ethylenediamino)-3,3,5,5-bis-spiro(N,N'-dinitroethylenediamino)cyclotriphosphazene*, **7**. To a refluxing solution of ethylenediamine (54 g, 900 mmol) in methylene chloride (150 mL) under inert

atmosphere was added dropwise a solution of **3** (12 g, 24 mmol) in methylene chloride (150 mL) over two hours. Additional methylene chloride (100 mL) was added and the resulting suspension was heated at reflux for a further 24 hours. The solvent was removed by rotary evaporation and the resulting residue was suspended in water. Product **7** was collected by filtration (9.0 g, 20 mmol, 84%), mp 245–249°C:

IR (KBr) 3450 (NH), 1550 (N—$NO_2$), 1275 (N—$NO_2$), 1230 $cm^{-1}$ (PNP); $^1H$ NMR (DMSO-$d_6$) $\delta$ 3.15 (d, 4H, $J_{H-P}$ = 12.6 Hz), $\delta$ 4.1 (d of m, 8H), $\delta$ 4.4 (d, 2H, $J_{H-P}$ = 14.6 Hz); $^{31}P$ (DMSO-$d_6$); $\delta$ 5.4 (d, $J_{P-P}$ = 56.6 Hz), $\delta$ 35.0 (t, $J_{P-P}$ = 56.6 Hz). HRMS m/e Calcd. for $(C_6H_{15}N_{13}O_8P_3)^+$ 490.0379. Found 490.0383.

*1,1,3,3,5,5-Tris-spiro(N,N'-dinitroethylenediamino)cyclotriphosphazene*, **8**.

*Method A*. A suspension of **7** (28.7 g, 58.6 mmol) in $CH_3CN$ (700 mL) was stirred at ice bath temperature and $NO_2BF_4$ (16.4 g, 123.5 mmol) was added to it over ten minutes. The resulting clear colorless solution was stirred at 0–5°C for 2 hours. The solvent was then removed under vacuum and the resulting yellow solid was immediately added to 500 mL of ice cold water. Continued stirring gave **8** as a faint-yellow solid (21.3 g, 36.9 mmol, 63%). This solid was washed with methanol (15 mL) and recrystallized from 5% aqueous acetone to give pure **8**, m.p. 203–205°C (dec). CAUTION: compound **8** exhibits explosive behavior on heating or when subjected to shock.

Alternatively, compound **8** was prepared by treating **7** with acetylnitrate. To 12 mL of 100% nitric acid cooled to −5°C was added dropwise with stirring 78 mL of acetic anhydride. The mixture was warmed to room temperature and stirred for an additional hour. It was then cooled to −5°C whence compound **7** (12.7 g, 25.9 mmol) was added at once. The resulting suspension was stirred at −5°C for one hour and then at room temperature for 3 hours more. The crude product was poured over ice (300 g), and the precipitated white product, **8**, (14.0 g, 24.1 mmol, 93%) was collected by filtration.

*Method B*. A stirred suspension of **9** (399 mg, 1.0 mmol) in $CH_3CN$ (30 mL) was cooled to 0°C and then $NO_2BF_4$ (671 mg of 84%, 5.0 mmol) was added all at once. The resulting solution was stirred at 0°C for 4 hours and then evaporated under vacuum to give a pale yellow oil. Addition of water (25 mL) precipitated a white solid which was filtered, washed with methanol, and dried to yield **8** (380 mg, 66%): mp 203–205°C (dec).

Compound **8** was also prepared by treating **9** with acetylnitrate. Nitric acid (3.0 g, 47.6 mmol of 100%) was added dropwise with stirring to acetic anhydride (7.39 g, 72.4 mmol) cooled to −5°C (salt-ice). The solution was then warmed to 20°C over 1 hour, cooled again to −5°C and to this was added **9** (1.197 g, 3.0 mmol) all at once. After stirring at −5°C for 2 hours the solution was poured onto a mixture of ice and water (150 mL) and the precipitated white solid filtered, washed with water (50 mL), then with methanol (25 mL) and dried to give **8** (1.595 g, 90%): mp 203–205°C (dec). Recrystallization from acetone-methanol gave colorless prisons: mp 205°C (violent dec).

IR (KBr) 1580 (N—$NO_2$), 1285 (N—$NO_2$), 1200 $cm^{-1}$ (PNP): $^1H$ NMR (acetone-$d_6$) $\delta$ 4.3 (m); $^{13}C$ NMR (acetone-$d_6$) $\delta$ 42.5 (d, $J_{C-P}$ = 9.8 Hz); $^{31}P$ NMR (acetone-$d_6$) $\delta$ 5.7 (s). HRMS CI ($NH_3$) m/e Calcd. 597.0346. Found: 597.0352. Anal. Calcd. for $C_6H_{12}N_{15}O_{12}P_3$: C, 12.44; H, 2.09; N, 36.28; P, 16.04. Found: C, 12.42; H, 2.02, N, 35.87; P, 16.09.

*1,1-spiro(N,N'-dinitroethylenediamino)-3,3,5,5-bis-spiro(ethylenediamino)cyclotriphosphazene*, **9**. A solution of ethylenediamine (3.60 g, 60 mmol) in $CH_2Cl_2$ (100 mL) was added dropwise over 1 hour to a stirred, refluxing solution of **5** (4.25 g, 10 mmol) in $CH_2Cl_2$ (50 mL). Refluxing was continued for an additional 24 hours, during which time a white solid precipitated. The mixture was cooled and the solid filtered, suspended in water (130 mL), and the pH brought to 9 by the addition of $NH_4OH$. After stirring for 30 minutes the solid was filtered, washed with water (50 mL), then acetone (20 mL), and dried to give **9** (3.67 g, 92%): mp 278–280°C (dec). The analytical sample, recrystallized from DMF, had mp 290°C (dec).

IR (KBr) 1540 (N—$NO_2$), 1280 and 1250 $cm^{-1}$ (N—$NO_2$ and/or PNP); $^1H$ NMR (DMSO-$d_6$) $\delta$ 3.97 (d, 4, $2CH_2$s), $\delta$ 3.77 (m, 4, NHs), $\delta$ 3.00 (m, 8, $4CH_2$s). Anal. Calcd. for $C_6H_6N_{11}O_4P_3$: C, 18.05; H, 4.04; N, 38.60; P, 23.28. Found: C, 18.42; H, 4.31; N, 38.11; P, 23.03.

*1,1,3,3-Bis-spiro(N,N'-dinitroethylenediamino)-5,5-diazidocyclotriphosphazene*, **10**. A stirred solution of **3** (3.20 g, 6.37 mmol) in DMSO (50 mL) wa cooled in a cold water bath during the addition of lithium azide (9.3 g, 0.19 mmol), in portions, over 5 minutes. The mixture was stirred at room temperature for 48 hours, then poured into cold water (200 mL), and the precipitate filtered and dried to yield **10** (2.35 g, 72%) as a white solid. Recrystallization from acetone-$H_2O$ gave colorless needles: mp 238°C (violent dec).

IR (KBr) 2182 ($N_3$), 1560 (N—$NO_2$), 1285 (N—$NO_2$), 1196 $cm^{-1}$ (PNP); $^1H$ NMR (DMSO-$d_6$) $\delta$ 4.08 (m, 4, $2CH_2$s), $\delta$ 4.26 (m, 4, $2CH_2$s); $^{31}P$ NMR (DMSO-$d_6$) $\delta$ 2.64 (d), $\delta$ 20.42 (t, $J_{P-P}$ = 63.3 Hz). Anal. Calcd. for $C_4H_8N_{17}O_8P_3$: C, 9.32; H, 1.57; N, 46.23; P, 18.04. Found: C, 9.67; H, 1.55; N, 46.22; P, 18.13.

*1,1-Spiro(N,N'-dinitroethylenediamino)-3,3,5,5-tetraazidocyclotriphosphazene*, **12**. Tetrazide **11** was prepared as described below from **4** and lithium azide in acetone. The crude oil (3.0 mmol) was dissolved in dry $CH_3CN$ (25 mL) and cooled in an ice-bath. With stirring, $NO_2BF_4$ (1.21 g of 84%, 9.0 mmol) was then added at once. After stirring at 0°C for 1 hour the solution was poured onto a mixture of ice and water (60 mL) and extracted with $CH_2Cl_2$. The extracts were washed twice with water, dried ($Na_2SO_4$) and then evaporated under vacuum to leave a solid residue which was triturated with cold ether and filtered to give **12** (545 mg, 40%): mp 144–145°C (colorless prisms from benzene-hexane).

IR (KBr) 2180 ($N_3$), 1565 (N—$NO_2$), 1300 (N—$NO_2$), 1270 and 1200 $cm^{-1}$ (PNP). $^1H$ NMR (acetone-$d_6$) $\delta$ 4.40 (m, $CH_2$). Anal. Calcd. for $C_2H_4N_{19}O_4P_3$: C, 5.32; H, 0.89; N, 59.00; P, 20.60. Found: C, 5.61; H, 0.93; N, 59.32; P, 20.45.

*1-(2-Ethylammonium)amino-1-oxido-3,3,5,5-tetraazidocyclotriphosphazene hemihydrate*, **13**. A mixture of **4** (5.02 g, 0.015 mmol) and powdered lithium azide (7.34 g, 0.15 mmol) in dry acetone (150 mL) was stirred at room temperature for 18 hours, then filtered. The filtrate was evaporated under vacuum to leave a mixture of oil and solid. The oil was dissolved in $CH_2Cl_2$ (50 mL), washed with $H_2O$ (2 × 25 mL), dried ($Na_2SO_4$) and then evaporated under vacuum to leave crude **11** (6.0 g) as a colorless oil.

IR (NaCl film) 2200 $cm^{-1}$ ($N_3$); $^1H$ NMR ($CDCl_3$) $\delta$ 3.53 (d, 4, $CH_2$), 2.77 (unsym.d, 2, NH).

This material was then dissolved in a mixture of $CH_3CN$ (40 mL) and $H_2O$ (10 mL) and allowed to stand at ambient temperature for 3 days, during which time a white solid precipitated. Filtration of the solid and drying gave **13** (5.01 g, 86%): mp 139–140°C (dec). Recrystallization from hot $CH_3CN$—$H_2O$ gave colorless needles: mp 140–141°C (dec).

$^{31}P$ NMR (DMSO-$d_6$) $\delta$ 4.45 (t), $\delta$ 12.33 (d, $J_{P-P}$ = 41.5 Hz). Anal. Calcd. for $C_2H_8N_{17}OP_3$ 0.5 $H_2O$: C, 6.19; H, 2.34; N, 61.35; P, 23.94. Found: C, 6.22; H, 2.49; N, 61.51; P, 24.22.

## X-RAY MEASUREMENT SECTION

Data for both analyses were collected on an automated Siemens R3m/V diffractometer equipped with a Mo X-ray tube ($\lambda$MoK$\alpha$) = 0.7103 Å) and an incident beam monochromator. The structures were solved and refined with the aid of the SHELXTL system of programs.[11]

*Single-crystal X-ray diffraction analysis of compound* **3**. F.W. = 502.0, orthorhombic space group $Pna2_1$, a = 16.372(3), b = 7.769(1), c = 13.811(2) Å, V = 1756.7(5) Å$^3$, Z = 4, $\rho_{calc}$ = 1.898 mg $mm^{-3}$, $\mu$ = 0.701 $mm^{-1}$, F(000) = 1008, T = 295°K. A clear colorless 0.33 × 0.44 × 0.55 mm crystal, in the shape of a truncated pyramid, was used. Lattice parameters were determined from 25 centered reflections within $28 \leq 2\theta \leq 30°$. The data collection range of *hkl* was: $0 \leq h \leq 19$, $-9 \leq k \leq 0$, $0 \leq l \leq 16$, with $[(\sin \theta)/\lambda]_{max}$ = 0.595. Three standards, monitored after every 97 reflections, exhibited random variations with devs. up to ±1.4% during the data collection. A set of 1817 reflections was collected in the $\theta/2\theta$ scan mode, with scan width $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$ and $\omega$ scan rate (a function of count rate) from 6°/min to 18°/min. There were 1623 unique reflections, and 1459 were observed with $F_o > 3\sigma(F_o)$. The full-matrix least-squares refinement varied 252 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model [coordinate shifts of C applied to attached H atoms, C—H distances set to 0.96 Å, H angles idealized]. The $U_{iso}$(H) were set to 0.080 Å$^2$. Final residuals were R = 0.058 and $wR$ = 0.063 with final difference Fourier excursions of 1.18 (near the P atoms) and −0.35 eÅ$^{-3}$.

*Single-crystal X-ray diffraction analysis of compound* **8**. F.W. = 579.2, monoclinic space group $P2_1/c$, a = 13.940(6), b = 13.699(5), c = 11.305(4) Å, $B$ = 109.07°, V = 2040(1) Å$^3$, Z = 4, $\rho_{calc}$ = 1.886 mg $mm^{-3}$, $\mu$ = 0.390 $mm^{-1}$, F(000) = 1176, T = 294°K. A clear colorless 0.15 × 0.20 × 0.65 mm crystal, in the shape of a rod, was used. Lattice parameters were determined from 25 centered reflections within $24 \leq 2\theta \leq 31°$. The data collection range of *hkl* was: $0 \leq h \leq 15$, $0 \leq k \leq 14$, $-12 \leq l \leq 11$, with $[(\sin \theta)/\lambda]_{max}$ = 0.538. Three standards, monitored after every 97 reflectionse exhibited a slow decline (2.5% corrected with a linear regression) during the data collection. A set of 3056 reflections was collected in the $\theta/2\theta$ scan mode, with scan width $[2\theta(K_{\alpha 1}) - 1.0]$ to $[2\theta(K_{\alpha 2}) + 1.0]°$ and $\omega$ scan rate (a function of count rate) from 3.0°/min to 15.6°/min. There were 2679 unique reflections, and 2212 were observed with $F_o > 3\sigma(F_o)$. The full-matrix least-squares refinement varied 327 parameters:

atom coordinates and anisotropic thermal parameters for all non-H atoms. H atoms were included using a riding model [coordinate shifts of C applied to attached H atoms, C—H distances set to 0.96 Å, H angles idealized]. The $U_{iso}$(H) were set to 0.081 Å$^2$. Final residuals were R = 0.053 and *w*R = 0.059 with final difference Fourier excursions of 0.42 and −0.38 eÅ$^{-3}$.

## CONCLUSIONS

Novel bis-spiroethylenedinitramino and tris-spiroethylenedinitramino derivatives of cyclotriphosphazenes have been synthesized in good yields and their structures confirmed by X-ray crystallography. The materials were found to have moderate impact sensitivity, high melting points, and excellent densities making this family of materials potentially useful in explosive compositions. These new energetic polynitraminocyclotriphosphazenes are the first examples of this novel class of compounds.

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